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Investigation of the in-solution relaxation of polymer optical fibre Bragg gratings

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Abstract: We investigate the response of PMMA microstructured polymer optical fibre Bragg gratings when immersed in methanol/water solutions. Overall we observe a permanent blue-shift in Bragg grating wavelength after solvent evaporation. The main contribution in the resonance wavelength shift probably arises from a permanent change in the size of the fibre, as already reported for high-temperature annealing of polymer optical fibres. As a consequence of the solution concentration dependence of the glass transition temperature of polymers, different methanol/water solutions lead to various degrees of frozen-in stress relaxation with an overall blue-shift of the Bragg grating wavelength.

Key Words: Polymer, Microstructured polymer optical fibre, Fibre Bragg grating, Annealing, Solution.

1. Introduction

Annealing of polymer optical fibre Bragg grating (POFBG) sensors has recently been the subject of an increasing number of studies as this process can enhance their thermal stability and widen the range of linear response of the gratings to temperature. Typical annealing conditions to obtain thermally stable hysteresis-free and wide operating range polymethyl methacrylate (PMMA) FBG sensors are 80°C and 90% RH [1]. The glass transition temperature (T_g) of a polymeric material equilibrated with a solvent differs from that of a pure polymer. Early investigations showed that the T_g of PMMA approaches room temperature when the polymer is equilibrated with methanol [2], whereas, at equilibrium with water, T_g is lowered by 20°C compared to pure PMMA [3]. This suggests that immersing a PMMA fibre in a suitable solution at room temperature may have an effect akin to annealing a solvent-free fibre at high temperature.

The aim of this work is to investigate the relaxation of PMMA mPOFBGs when immersed in methanol/water solutions. As a consequence of the solution concentration dependence of the T_g of PMMA, varying methanol/water ratio implies changing the T_g of a PMMA FBG when equilibrated with the solution, which results in a different degree of frozen-in drawing stress relaxation.

2. In-solution relaxation

The T_g of a polymer equilibrated with a solvent in general differs from the one for a solvent-free polymer. Early studies by Williams et al. [2] investigated the effect of presence of methanol on the T_g of PMMA. Depending on the weight-average molecular weight (M_w), the reported values for methanol-equilibrated PMMA systems range from 20°C ($M_w = 23500$ g/mol) to 30°C ($M_w = 550000$ g/mol), where M_w can be thought of as an average length of the polymer chain. PMMA polymers optimal for fibre drawing processes have an M_w of about 60000 g/mol [4]. This means that the T_g of a methanol-equilibrated PMMA fibre is around room temperature. Annealing is typically required for extending the temperature operating range of POFs and POFBGs as a polymer fibre tends to relax drawing stresses when it is heated up to high temperature (i.e., a temperature non far from their T_g). This can affect the dimensional stability of the fibre and therefore limit its operating temperature to values well below the theoretical ones. Heating up an un-annealed fibre to even modest temperatures may cause a permanent (blue-)shift in the Bragg reflection wavelength, and also its optical and mechanical properties may be affected. The fibre drawing process aligns the polymer chains in the draw direction to an extent mainly depending on the applied drawing forces. This leads to frozen-in stresses in the final fibre. Indeed, as a result of the fibre drawing process, polymer chains are in a non-equilibrium state and tend to move back towards the original configuration as soon as they are provided with enough energy to do so. The higher the temperature the greater the energy available for the polymer chains to rearrange themselves. This relaxation typically has the effect of changing the dimensions (i.e. length and diameter) of a

fibre. If we consider that approaching T_g is the condition required for the relaxation to occur, we can theoretically obtain an effect similar to annealing if we lower the T_g of the polymer fibre by immersing it in a methanol-based solution at room temperature. Pure methanol has been already used for the doping of PMMA POF canes with various compounds, e.g. Rhodamine 6G [5] and benzyl dimethyl ketal (BDK) [6]. Nevertheless, pure methanol cannot be directly used for stress relaxation in PMMA mPOFBGs as it corresponds to a too high annealing temperature. Hence we used water to dilute methanol. Water (Milli-Q) was chosen as it is miscible with methanol and the T_g of water-saturated PMMA was known from the literature to be approximately 20°C lower than that of the pure polymer [3]. So that we could expect that the addition of water would increase the T_g of PMMA equilibrated with a methanol/water solution, starting from a T_g being around room temperature when pure methanol is used.

3. Experiments and results

The PMMA mPOF was made by using the drill-and-draw method [4]. The average diameter of the fibre was around 150 μm . The fibre was two-ring microstructured with an 8 μm core. The hole pitch and hole diameter were 5 μm and 2 μm , respectively. The fibre was single-mode as the hole to pitch ratio was 0.40. Bragg gratings were inscribed into the fibre by using a CW HeCd laser operating at 325 nm (IK5751I-G, Kimmon). For grating writing the phase mask method was used. The inscription setup was the same as in Bundalo et al. [7]. The laser power for grating writing was 20 mW. A custom-made phase mask by Ibsen Photonics A/S was used, optimised for writing at 325 nm and having a uniform period of 572.4 nm. Two FBGs were inscribed in two PMMA mPOFs from the same fibre draw and tested in solutions at two different methanol/water concentrations, 60:40% and 70:30% v/v. The initial resonance wavelengths (before immersion) were 846.2 nm and 847.3 nm, respectively. CHROMASOLV methanol (for HPLC, $\geq 99.9\%$, Sigma-Aldrich) and Milli-Q water were used in the experiments. In both cases, 10 ml solutions were prepared in 10 ml graduated cylinders sealed at the top to avoid evaporation throughout the experiments. The FBGs were removed from the solution once the rate of Bragg reflection wavelength shift (absolute value) was around 0.55 nm/hour.

Figure 1 shows the Bragg grating wavelength of a PMMA mPOFBG immersed in a solution of methanol and water 60:40% v/v for 33 hours. After the stopping criterion was met, the FBG was removed from the solution and monitored for further 9 hours in order to study the grating response during solvent evaporation. In this experiment we observed an overall blue-shift of 82.0 nm.

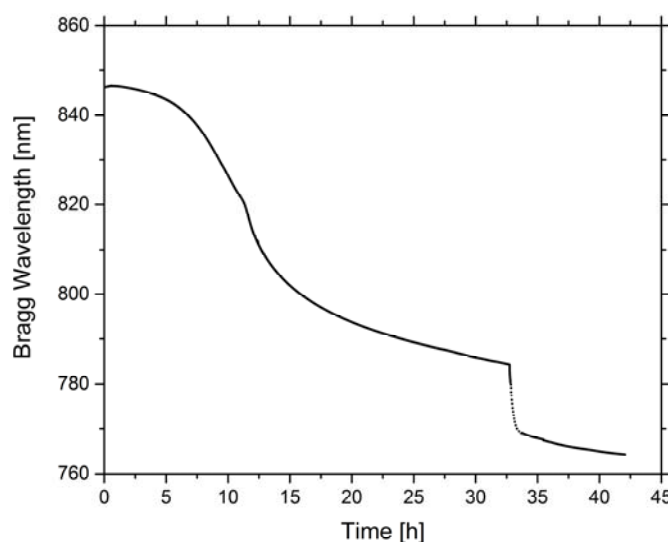


Figure 1. PMMA mPOFBG resonance wavelength monitored over 42 hours (immersion time = 33 hours). The solution is methanol/water 60:40% v/v. Two distinct regions can be observed: absorption-relaxation (0-33 hours) and desorption (33-42 hours). Note that a few experimental data were missing due to high reflection noise. Hence, in that region of the graph the curve was fitted (dotted line).

The absorption of the methanol/water solution in general changes both refractive index and fibre size. Since the shift was permanent, the relaxation probably corresponds to a permanent change in the size of the fibre, as already observed in high-temperature annealing of polymer optical fibres [8]. Some initial red-shift in Bragg wavelength was observed, with a maximum of +0.3 nm. This was the results of a temporary positive balance between red-shift due to solution-mediated swelling and blue-shift caused by chain alignment relaxation. However, after about 100 minutes the total shift referred to the initial Bragg wavelength became constantly negative. This corresponds to the tendency towards relaxation becoming stronger and stronger after an initial lag phase due to the initial diffusion of the solution into the fibre. However, the real contribution due to absorption/swelling, which would lead to a much greater red-shift than the observed one, was hidden by the incipient relaxation (blue-shift). This can easily be seen from Fig. 1, where a sudden and very sharp blue-shift of the resonance wavelength corresponding to a very fast solvent evaporation upon FBG removal from the solution is shown (time = 33 hours). The fast evaporation process was probably facilitated by the small diameter of the fibre (150 μm). The further down-shift occurred after removal of the Bragg grating from the solution was measured to be -20.2 nm (time = 42 hours). The shift was towards blue as evaporation implied de-swelling of the methanol/water solution, which caused further fibre shrinkage. The mild decrease observed after the sharp downward jump in resonance wavelength was probably due to solvent evaporation and some residual relaxation becoming less and less important as the solvent evaporation went on. An overall shift of -82.0 nm is comparable with the effect of 80 $^{\circ}\text{C}$ and 30% RH annealing conditions on PMMA mPOFBGs as reported by Woyessa et al. [1]. We further repeated the experiment applying similar conditions to a PMMA mPOF from the same draw in order to measure the total fibre shrinkage. The corresponding fibre shrinkage was measured to be about 8%.

Figure 2 shows the Bragg grating wavelength versus time for a PMMA mPOFBG immersed in a solution methanol/water 70:30% v/v. After 24 hours the FBG was removed from the solution (sharp downward jump in Fig. 2) and monitored for further 9 hours during evaporation as done for the case 60:40% v/v. As expected, the effect on the reflection wavelength was more pronounced, as a total blue-shift of 113.8 nm was recorded. Notice, the final resonance wavelength of 733.5 nm approximately corresponds to the resonance wavelength obtainable when the annealing of 850 nm PMMA mPOFBGs is performed at 80 $^{\circ}\text{C}$ and 70% RH [1].

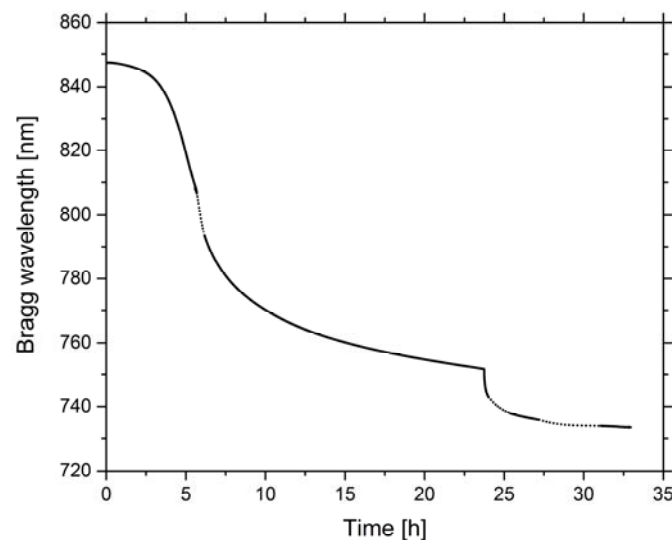


Figure 2. PMMA mPOFBG resonance wavelength monitored over 33 hours (immersion time = 24 hours). The solution is methanol/water 70:30% v/v. Two distinct regions may be seen: absorption-relaxation (0-24 hours) and desorption (24-33 hours). As happened in the case 60:40% v/v, some data were missing because of high reflection noise and were therefore obtained by non-linear fitting (dotted lines).

Unlike the previous case of methanol/water 60:40% v/v, we did not observe any significant initial red-shift when using methanol/water 70:30% v/v. Also, the relaxation process was visibly faster as methanol is a stronger swelling agent for PMMA than is water. The total blue-shift in resonance wavelength measured from FBG removal from the solution (time = 24 hours) until the end of the experiment (time = 33 hours) was 18.4 nm, comparable with the previous experiment. As done in the case 60:40% v/v, we repeated the experiment on the PMMA mPOF to evaluate the corresponding fibre shrinkage. The overall shrinkage for the same fibre after being immersed in a solution methanol/water 70:30% v/v for the same time and left dry was approximately 16%.

4. Conclusion

The possibility of relaxing stresses frozen in the fibre by using methanol/water solutions was demonstrated. A tunability up to 82.0 nm and 113.8 nm was shown for solutions methanol/water 60:40% v/v and 70:30% v/v, respectively. Both blue-shifts were permanent and obtained at room temperature by immersing two-ring PMMA mPOFBGs in a methanol-based solution at various concentrations of water. This suggests that solution stress relaxation may represent a viable process to improve the thermal stability of PMMA mPOFBGs as an alternative to conventional annealing. In addition, with an appropriate combination of solvents, the same principle could also be applied to other polymers, such as TOPAS and polycarbonate. This solution-based method could be particularly advantageous when thermally activated degradation processes associated with long exposure times at high temperature are an issue. Moreover, it may represent a cheap way of annealing as no complex and expensive climate chamber is required.

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